

I.

**The Detection and Determination of Minute  
Quantities of Glycerine**

II.

**The Volumes of Weight-Normal Cane Sugar  
Solutions at Different Temperatures**

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**DISSERTATION**

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF  
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY  
WITH THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY.

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BY  
FELTON SAMUEL DENGLE,  
BALTIMORE,  
1912

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GEORGE W. KING PRINTING CO.  
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To Dr. Frazer and Dr. Holland the author's thanks are due for willing assistance.





## PART 1.

### *The Detection and Determination of Minute Quantities of Glycerine.*

In the measurement of osmotic pressure in this laboratory, no measurement is regarded as conclusive until it has been shown that the membrane was not broken, thereby allowing some of the solution to escape from the cell. In other words, the solution whose osmotic pressure is being measured must have the same concentration after the cell has been up days, or in some cases weeks, as it had when it was first put up. There are two ways of solving this problem. Either the solution on the inside of the cell must be tested before and after the experiment, to ascertain whether or not any dilution has taken place, or the solution on the outside of the cell must be tested to ascertain whether or not it contains any of the substance whose osmotic pressure is being measured.

The polarimeter affords an excellent method for substances which are optically active, but in the case of glycerine, it was thought more practicable to test the water in which the cell is immersed for the presence of this substance. It was necessary to search for some methods for the detection and determination of minute quantities of this substance.

#### *Qualitative Test.*

In the measure of osmotic pressure, it is the practice here to make the water in which the cell is immersed during measurement, one-hundredth ion weight normal with copper sulphate; while to the solution on the inside of the cell, there is added, besides the substance whose osmotic pressure is to be determined, a quantity of potassium ferro cyanide, which is osmotically equivalent to the copper sulphate on the outside. The purpose of the addition of these membrane-forming salts, is to

repair any break which may occur in the membrane. If there is added to an alkaline solution of glycerine, a small quantity of copper sulphate, the solution becomes deep blue in color, but without precipitation of cupric hydroxide. If the addition of copper sulphate is continued, the precipitate of cupric hydroxide appears. The color is very similar to the color of solutions containing the  $\text{Cu}(\text{NH}_3)_4$  ion.

The cupric hydroxide can be filtered off through an asbestos filter, although some of the colored copper glycerine compound is absorbed by the asbestos in the filtering process. Because this absorption takes place, the method cannot be used for the quantitative determination of small quantities of glycerine colorimetrically.

It was a question whether or not this color might be due to the alkali dissolving some of the copper, hence the experiments tabulated below were carried out to determine at what concentration the alkali dissolves the copper. Column 2 shows the quantities of copper sulphate; column 3, the quantities of glycerine; column 4, the quantities of potassium hydroxide; column 5, the total number of cubic centimeters in the final solution; column 6, is the normality of the alkali obtained from columns 4 and 5, and column 7 shows the color of the filtrate.

| 1        | 2                            | 3            | 4           | 5                | 6                  | 7                    |
|----------|------------------------------|--------------|-------------|------------------|--------------------|----------------------|
| Exp. No. | Cu<br>SO <sub>4</sub><br>mg. | Glyc.<br>mg. | KOH.<br>mg. | Total No.<br>cc. | KOH.<br>Normality. | Filtrate.            |
| 1        | 24.78                        | 5            | 28.05       | 21               | .023               | no color             |
| 2        | 24.78                        | 5            | 280.50      | 30               | .170               | slight color         |
| 3        | 24.78                        | 5            | 420.75      | 35               | .210               | slight color         |
| 4        | 24.78                        | 5            | 504.90      | 38               | .240               | good color           |
| 5        | 24.78                        | 5            | 701.25      | 45               | .280               | deep color           |
| 6        | 24.78                        | 0            | 701.25      | 45               | .280               | slight color         |
| 7        | 24.78                        | 0            | 701.25      | 45               | .280               | slight color         |
| 8        | 24.78                        | 0            | 420.75      | 35               | .210               | no color             |
| 9        | 24.78                        | 0            | 504.00      | 38               | .240               | no color             |
| 10       | 24.78                        | 0            | 561.00      | 40               | .250               | very<br>slight color |
| 11       | 49.56                        | 5            | 504.90      | 38               | .240               | good color           |
| 12       | 49.56                        | 0            | 504.90      | 38               | .240               | no color             |



A study of the table shows that in the first five experiments, as the concentration of the alkali increases—the quantities of all the other substances being kept constant—from .23 normal to .28 normal, the color of the filtrate increases. Experiments Nos. 6 and 7, which contain no glycerine, show by the slight color of the filtrate that some of the copper has been dissolved. In experiments 8 and 9, in which the concentration of the alkali was .21 and .24 normal, respectively, no color was obtained in filtrate, while in experiment No. 10, when the alkali was .25 normal, a very slight color was obtained in the filtrate. Some of the copper is dissolved then when the alkali is .25 normal, but it is not dissolved if the alkali is kept at .24 normal, or below. In other words, the solution in which this reaction is employed for the detection of glycerine must not be over .24 normal with potassium hydroxide.

The following experiments were carried out with the view of determining how small quantities of glycerine could be detected:

| Glyc.<br>mg. | Cu SO <sub>4</sub><br>mg. | Normality,<br>Cu SO <sub>4</sub><br>N | KOH<br>mg. | Normality<br>KOH | Total No.<br>cc. | Filtrate. |
|--------------|---------------------------|---------------------------------------|------------|------------------|------------------|-----------|
| 5            | 123.92                    | 100                                   | 1262.25    | .23              | 100              | colored   |
| 3            | 123.92                    | 100                                   | 1262.25    | .23              | 100              | colored   |
| 2            | 123.92                    | 100                                   | 1262.25    | .23              | 100              | colored   |
| 1            | 123.92                    | 100                                   | 1262.25    | .23              | 100              | colored   |
| 0            | 123.92                    | 100                                   | 1262.25    | .23              | 100              | colorless |

These show that one milligramme of glycerine can be detected in one hundred cubic centimeters of solution. The filtrate of the blank containing no glycerine is colorless, therefore the color in the other experiments can not be due to dissolve copper.

Some idea of the composition of the copper-glycerine compound was obtained by mixing copper sulphate and glycerine in different proportions, molecule for molecule. If all the copper

is used up by the glycerine in forming the colored compound, then no precipitate of cupric hydroxide will be formed. A precipitate then indicates that more copper is present than is necessary for the formation of the colored compound.

|                                                                | glyc.<br>mg. | Cu SO <sub>4</sub><br>mg. | Normality<br>KOH | Total No.<br>cc. |                                |
|----------------------------------------------------------------|--------------|---------------------------|------------------|------------------|--------------------------------|
| 1 mol. glyc. to $\frac{1}{2}$ mol.<br>CU SO <sub>4</sub> ..... | 2            | 2.71                      | .23              | 100              | Slight color and no ppt.       |
| 1 mol. glyc. to $\frac{1}{2}$ mol.<br>CU SO <sub>4</sub> ..... | 3            | 4.07                      | .23              | 100              | Good color and no ppt.         |
| 1 mol. glyc. to 1 mol.<br>CU SO <sub>4</sub> .....             | 3            | 8.13                      | .23              | 100              | Good color and a ppt.          |
| 1 mol. glyc. to 1 mol.<br>CU SO <sub>4</sub> .....             | 100          | 271.2                     | .23              | 100              | Deep blue color and ppt.       |
| 1 mol. glyc. to $\frac{1}{2}$ mol.<br>CU SO <sub>4</sub> ..... | 100          | 135.62                    | .23              | 100              | Deep blue color and no<br>ppt. |

The experiments show that when the ratio is one molecule of glycerine to one-half molecule of copper sulphate, or rather two molecules of glycerine to one molecule of copper sulphate, then all the copper remains in solution. The conclusion to be drawn from these facts is that the copper atom substitutes two hydrogen atoms, each in different molecules of glycerine, and thus serves to hold together two glycerine residues. The logical way to carry out these experiments would be to add the copper sulphate solution drop by drop to the alkaline glycerine solution until one drop produces a precipitate of cupric hydroxide. This was tried, but a precipitate appeared before the ratio reached two molecules of glycerine to one molecule of copper sulphate. It would appear then that some of the copper was used up by the alkali to form cupric hydroxide before all the glycerine had been changed to the colored compound. The alkali must then be added last to the solution containing the copper sulphate and the glycerine.

The qualitative test can then be used for detecting two or three milligrammes, and with some experience, one milligramme of glycerine in one hundred cubic centimeters of solution. The



unknown solution should contain enough copper sulphate to make it one-hundredth normal, and enough alkali is then added to make the solution .23 normal. The precipitate of cupric hydroxide is filtered off, and if the filtrate has a blue color, the solution contained glycerine, provided other substances are absent which behave in the same way.

### *Quantitative Determination.*

The estimation of glycerine can be affected by oxidation with potassium permanganate or potassium dichromate. Hehner's<sup>1</sup> dichromate method, in which the amount of that salt reduced is determined, has this objection, that since the standard solution is somewhat strong and expands as much as .05 per cent. per degree, great care must be taken to keep the temperature constant, and at best, the method does not permit any great refinement and was wholly inapplicable to our purpose.

The permanganate oxidation method was first proposed by Wauklyn,<sup>2</sup> and further worked by Fox, Benedikt and Zsigmondy.<sup>2</sup> The following is a brief statement of the same: The glycerine solution is made alkaline with potassium hydroxide and then treated with a saturated solution of permanganate. The solution is boiled one hour and then treated with enough sodium sulphite to destroy the excess of permanganate. The precipitated manganese dioxide is filtered off, and known volumes of the filtrate are acidified with acetic acid and then treated with calcium chloride. The precipitated calcium oxalate is either determined gravimetrically as the carbonate or the precipitate is rinsed from the filter, acidified with sulphuric acid, heated to 60 degrees C. and titrated with a decinormal solution of permanganate. The authors of the method obtained satisfactory results with it, but it is long and rather complicated. The method was likewise inapplicable where very minute quantities of glycerine were to be determined.

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1. Allen's Commercial Organic Chemistry. Vol. 2, 316.

2. Allen's Commercial Organic Chemistry. Vol. 2, 314.

The following work was undertaken then to adapt the oxidation by permanganate to our conditions. The standard solution of potassium permanganate employed contained from five to six milligrammes of the dissolved salt in each cubic centimeter. A standard solution of potassium tetroxalate, which was used in determining the strength of the permanganate, was made equivalent, as nearly as possible, to the permanganate solution.

Solutions of potassium permanganate are not stable and often deteriorate very rapidly because of the reduction caused by small quantities of the oxides of manganese. The best results were obtained by preparing the permanganate solution in the following way: The approximate amount of the salt is dissolved in water and allowed to stand in the dark for several days. This gives a chance for the oxidation of any oxidizable substance, and also any precipitated oxides are coagulated. The solution is then filtered through two connected asbestos filters. The filtrate is then allowed to stand for several more days and then filtered by the same process into a clean bottle. The necessary amount of water can then be added. Solutions prepared in this way can be kept two weeks or more without any appearance of oxide or any deterioration.

The potassium tetroxalate was prepared in the usual way. A saturated solution of oxalic acid was divided into two parts. The smaller part was one-fourth of the whole, less about two or three cubic centimeters. The smaller portion was neutralized with potassium carbonate while boiling. The larger portion was then heated and the potassium oxalate stirred in. The crystals obtained are then recrystallized twice from water and dried on porous plates.

All the oxidation experiments were carried out in alkali solutions. The solutions also contained enough copper sulphate to make them one-hundredth normal with respect to that sub-

stance. Preliminary experiments were necessary to determine the time and temperature necessary for the complete oxidation. The best results were obtained by keeping the solutions for nineteen hours in a constant temperature bath regulated at 50 degrees C. Increasing the time did not increase the amount of permanganate reduced.

An experiment was carried out in the following way: To an alkaline solution of copper sulphate and glycerine, a considerable excess of standard potassium permanganate solution is added. This is then allowed to stand in the 50 degree bath for nineteen hours. To this is then added potassium tetroxalate equivalent to the amount of potassium permanganate used. The solution, after reduction, is then acidified with sulphuric acid, heated to 60 degrees C., and titrated with potassium permanganate solution until a pink color is obtained. The amount of potassium permanganate used in titrating is equivalent to the amount of potassium permanganate reduced by the glycerine. The number of atoms of oxygen, equivalent to the amount of potassium permanganate reduced, was then calculated, and from this the number of atoms of oxygen per molecule of glycerine determined. Blank experiments were put in every day, which were in every respect identical with the other experiments, except that they contained no glycerine. By means of these blank experiments any reduction outside of that produced by the glycerine itself, could be detected and they also serve as a check on the strength of the potassium permanganate solution. In every instance where a reduction had apparently taken place in these blank experiments, it was found that the potassium permanganate solution had deteriorated.

The following oxidation experiments were all kept in a 50 degree constant temperature bath for nineteen hours. The results are calculated in terms of the number of atoms of oxygen per molecule of glycerine. The theoretical number of atoms of oxygen necessary to oxidise a molecule of glycerine to carbon dioxide and water is seven.



| 1        | 2            | 3                         | 4          | 5                                 | 6                                | 7                                        | 8                            |
|----------|--------------|---------------------------|------------|-----------------------------------|----------------------------------|------------------------------------------|------------------------------|
| Exp. No. | Glyc.<br>mg. | Cu SO <sub>4</sub><br>mg. | KOH<br>mg. | K Mn O <sub>4</sub><br>mg. added. | K Mn O <sub>4</sub><br>mg. used. | mg. K Mn O <sub>4</sub><br>per mg. Glyc. | Atoms of O<br>per mol. Glyc. |
| 1        | 1            | 123.9                     | 140        | 248.73                            | 5.29                             | 5.29                                     | 7.68                         |
| 2        | 1            | 123.9                     | 140        | 248.73                            | 5.47                             | 5.47                                     | 7.96                         |
| 3        | 2            | 123.9                     | 140        | 248.75                            | 9.33                             | 4.66                                     | 6.79                         |
| 4        | 2            | 123.9                     | 140        | 248.75                            | 9.33                             | 4.66                                     | 6.79                         |
| 5        | 5            | 123.9                     | 140        | 248.75                            | 23.63                            | 4.73                                     | 6.87                         |
| 6        | 5            | 123.9                     | 140        | 248.75                            | 24.06                            | 4.81                                     | 7.00                         |
| 7        | 10           | 123.9                     | 140        | 248.75                            | 46.76                            | 4.66                                     | 6.80                         |
| 8        | 10           | 123.9                     | 140        | 248.75                            | 46.64                            | 4.66                                     | 6.79                         |
| 9        | 25           | 123.9                     | 140        | 248.75                            | 117.17                           | 4.69                                     | 6.81                         |
| 10       | 25           | 123.9                     | 140        | 248.75                            | 116.78                           | 4.67                                     | 6.79                         |
| 11       | 30           | 123.9                     | 140        | 249.40                            | 141.04                           | 4.70                                     | 6.84                         |
| 12       | 30           | 123.9                     | 140        | 249.40                            | 140.47                           | 4.68                                     | 6.82                         |
| 13       | 30           | 123.9                     | 140        | 249.40                            | 140.85                           | 4.70                                     | 6.84                         |
| 14       | 40           | 123.9                     | 140        | 311.75                            | 185.78                           | 4.64                                     | 6.76                         |
| 15       | 40           | 123.9                     | 140        | 311.75                            | 185.97                           | 4.65                                     | 6.77                         |
| 16       | 40           | 123.9                     | 140        | 311.75                            | 187.45                           | 4.69                                     | 6.82                         |
| 17       | 50           | 123.9                     | 140        | 446.01                            | 234.79                           | 4.70                                     | 6.84                         |
| 18       | 50           | 123.9                     | 140        | 446.01                            | 235.75                           | 4.71                                     | 6.86                         |
| 19       | 50           | 123.9                     | 140        | 446.01                            | 233.84                           | 4.68                                     | 6.81                         |
| 20       | 48.5         | 123.9                     | 140        | 498.80                            | 224.46                           | 4.63                                     | 6.74                         |
|          |              |                           |            | Mean                              |                                  | 4.69                                     | 6.82                         |

Columns 2, 3 and 4 show the quantities of glycerine, copper sulphate and alkali in each experiment. Column 5 shows the quantity of permanganate added for the oxidation of the glycerine. A large excess of permanganate must be added, since in alkaline solution, only one and a half atoms of oxygen per molecule of permanganate are available for oxidizing the glycerine. Column 6 shows the amount of permanganate reduced by the quantity of glycerine in column 1. Column 7 gives the milligrammes of permanganate reduced by each milligramme of glycerine. Column 8 gives the number of atoms of oxygen for each molecule of glycerine calculated from the quantity of permanganate reduced, and the quantity of glycerine present.

The mean values do not include experiments 1 and 2, where only 1 milligramme of glycerine was oxidized. The mean number of atoms per molecule of glycerine is 6.82, while the theoretical number is seven. Two different solutions of glycerine were used in these experiments, one containing one milli-

gramme of glycerine per cubic centimeter of solution, and the other contained five milligrammes of glycerine per cubic centimeter of solution, so that it was unlikely there was an error in making up the glycerine solution. As a further check on the glycerine solution in experiment No. 20, a weighed amount of glycerine was oxidized directly with practical agreement. In experiments Nos. 1 and 2, the results obtained are high compared with others. This is probably due to the experimental errors, including the temperature effects on standard solutions, which are often considerable, accumulating on the small quantity of glycerine.

In view of the fact that all the results obtained are below in the amount of oxygen necessary to oxidize the glycerine to carbon dioxide and water, it seemed desirable to check this method by some other method. It was first proposed to oxidize the glycerine with chromic acid, and collect the carbon dioxide gas formed, and in this way determine the purity of the glycerine. This method did not work out, as the chromic acid seemed to absorb the carbon dioxide, and the results were lower than those obtained by the potassium permanganate method.

The electrical method for the combustion of organic substances devised by Morse, Taylor and Gray<sup>1</sup> was then used. The glycerine was burned in a current of heated oxygen. The oxygen is heated by passing through a porcelain tube around which a platinum wire is coiled, and which wire carries a current of electricity. The results of five combustions are contained in the following table:

| Glyc.<br>mg. | CO <sub>2</sub><br>mg. | Theoretical<br>Carbon mg. | Carbon<br>Found mg. | Deficit<br>Carbon mg. | Atoms of O<br>per mol. of<br>Glyc. |
|--------------|------------------------|---------------------------|---------------------|-----------------------|------------------------------------|
| 98.0         | 137.7                  | 38.318                    | 37.551              | 0.767                 | 6.85                               |
| 81.0         | 112.4                  | 31.671                    | 30.651              | 1.020                 | 6.78                               |
| 74.9         | 103.7                  | 29.286                    | 28.279              | 1.007                 | 6.76                               |
| 80.2         | 112.8                  | 31.358                    | 30.761              | .598                  | 6.87                               |
| 87.1         | 122.3                  | 34.056                    | 33.351              | .705                  | 6.86                               |
|              |                        |                           |                     | Mean=                 | 6.82                               |

1. Morse, "Exercises in Quantitative Chemistry," page 537.

The results obtained then by the potassium permanganate and electrical combustion methods agree, and the glycerine used has a purity of 97.29%. The glycerine oxidized by the permanganate was therefore only 97.29 per cent pure. If we apply this correction to 6.82, the mean number of atoms of oxygen which appear to be used by a molecule of glycerine, we get 7.01 atoms of oxygen per molecule of glycerine, while the theoretical number is seven. Glycerine is very hygroscopic, and in all operations care was taken so that the substance was exposed as little as possible to the moisture of the air.

The potassium permanganate oxidation method then can be used for determining quantities of glycerine as small as two milligrammes in alkaline copper sulphate solutions.

The solutions inside and outside the cell are in ordinary practice, made one-thousandth normal with thymol to prevent the growth of penicillium in the sugar solutions. If the potassium permanganate method is used for the quantitative determination of the glycerine, some other way of destroying the penicillium will have to be devised. The thymol is readily oxidized by the permanganate, and the amount of permanganate reduced by the thymol would be large compared to the amount reduced by glycerine, so that all the experimental errors would accumulate on the relatively small quantity of that substance.



## PART 2.

### *Volumes of Weight Normal Cane Sugar Solutions at Different Temperatures.*<sup>1</sup>

When a solid substance is dissolved in a liquid, the volume of the solution is not equal to the sum of the volumes of the solute and solvent, but is usually smaller. This shrinkage is often quite large, and in the case of weight normal solution of glucose, it was found by Morse, Frazer and Dunbar<sup>2</sup> to be 6.03 cubic centimeters,\* when 178.74 grams of glucose are dissolved in 1,000 grams of water at 0 degrees. The exact nature of the cause of this contraction is not known.

This investigation was undertaken with the view of determining the contraction in cane sugar solutions at different temperatures. It was proposed to measure the increase in volume directly in going from a lower to a higher temperature. In other words, the apparatus was to be of the dilatometer rather than the pycnometer type. With this in view, an apparatus illustrated in Figure 1 was devised.

It consists essentially of a bulb and a calibrated tube "ab," in which the increase in volume is read with the cathetometer. The stop cock is placed at the bottom for convenience in cleaning and drying the apparatus. It also has the advantage that no small gas bubbles can collect there when the temperature is

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1. This work was done in collaboration with Mr. Eysell, and all the data on the odd concentrations will be found in his dissertation.

2. Am. Chem. Journal, 38, 222.

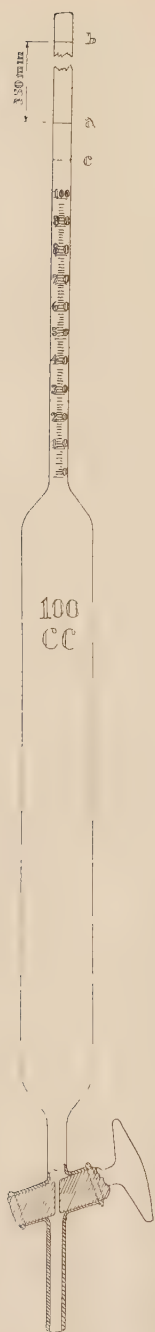


FIGURE 1.

raised, which might happen were it placed on the side or near the top. It is, of course, necessary that the stop cock fit perfectly, and considerable grinding was necessary in order to obtain the desired result.

The bulb part and the capillary tube "ab" are prepared separately and then sealed at "c." The bulb is weighed empty. It is then filled with air-free water of known temperature to the 0 mark on the tube and weighed. It is then filled with water of a known temperature to the 100 mm. mark, and again weighed. From the weights and temperatures of the water, the capacity of the bulb to 0 mark and of the tube from 0 to 100mm. can be calculated. The small tube "ab" has an internal diameter of 2.225 mm., and the distance between the scratches "a" and "b" is approximately 350 mm. The part between the scratches was carefully calibrated by means of a short thread of mercury, and a curve drawn for the corrections which must be applied on account of the inequalities of the bore. The calibrated tube was then sealed on to the graduated tube at "c." The capacity between the 100 mm. mark and the lower scratch "a" was determined by means of a mercury thread which rested on the 100 mm. mark and extended above scratch "a" into the calibrated part of the tube. The thread was weighed and its volume calculated at the temperature. The known volume of the portion of the tube above the scratch "a" which is filled by the mercury, is then deducted from the total volume. The difference, after applying the meniscus correction, is the capacity of the apparatus between "a" and the upper limit of graduation. All weighings were made with a tare of the same volume and form, so that the weighings were not influenced by temperature, moisture or air displaced. In all, eleven such pieces of apparatus were prepared so that ten could be used for the ten weight normal cane sugar solutions, and the eleventh for air free water.

The water used in making up the cane sugar solutions was boiled to free it from air. In making up a solution, the quantity of water was taken, which in a vacuum, would weigh 150 grams.



To this was added the necessary weight of cane sugar, also corrected for air displaced. The rotation of the solution was taken with a polarimeter as a check on the concentration. The rotation was also taken after the experiment, in order to determine whether any increase or loss of concentration had taken place. The cane sugar solution was cooled below the temperature of the bath in order that there might be an increase rather than a decrease in volume in reaching the temperature of the bath. A decrease in volume would mean the leaving of a film of solution on the walls of the calibrated tube, and the exact volume would necessarily be diminished by that amount. The top of the calibrated tube was closed by means of a rubber cap used in fountain pen fillers. This cap effectually prevented any evaporation, and at the same time allowed for any expansion.

The temperature of the hydrant water during April, made it necessary to give up all the temperatures below 15 degrees. The pieces of apparatus were weighed empty, filled with the solutions, and placed in a constant temperature bath regulated automatically to keep the desired temperature with a maximum variation of about .01 of a degree. A description of the bath used will be found in Vol. 45 of the American Chemical Journal, page 381. Several days were required for the solutions and glass to come to temperature, after which constant readings were obtained on the height of the liquid in the calibrated tube. After the volumes of the solutions had remained constant for several days and the necessary readings secured, the bath was regulated to the next desired higher temperature. In this work, the volumes were determined at 15, 20, 25, and 30 degrees. The pieces of apparatus were then taken down and weighed with the contained solution. From the weight of the apparatus, empty and full, the weight of the solution is obtained. This weight must be corrected for the weight of the solution contained in the bore of the stop cock, since this solution in the stop cock did not enter into the volume changes. The correction was applied as follows: The volume of the bore of the stop cock was determined by means of mercury. This volume

was then added to the observed volume of the whole solution at 20 degrees. The weight of the solution, divided by this corrected volume, gives the density of the solution. The density times the volume of the bore of the stop cock, gives the weight of the solution in the stop cock, and this weight, subtracted from the original weight, gives the corrected weight of the solution in the tube. In the following table 1, column 1, contains the number of the pieces of apparatus; column 2, the weight normal concentration of the solution; column 3, the volume of the bore of the stop cock; column 4, the density of the solution; column 5, the weight of the solution in the bore, and column 6, the corrected weight of the solution in the apparatus.

TABLE 1.

| 1        | 2                   | 3                                   | 4                          | 5                           | 6                                          |
|----------|---------------------|-------------------------------------|----------------------------|-----------------------------|--------------------------------------------|
| App. No. | Weight normal conc. | Volume of, bore of stop-cock in cc. | Density of sugar solution. | Weight of solution in bore. | Corrected weight of solution in apparatus. |
| 7        | 0.2                 | .0510                               | 1.0228                     | .0522                       | 102.6412 g.                                |
| 13       | 0.4                 | .0576                               | 1.0458                     | .0602                       | 105.1192 g.                                |
| 6        | 0.6                 | .0393                               | 1.0663                     | .0419                       | 107.2322 g.                                |
| 10       | 0.8                 | .0472                               | 1.0869                     | .0513                       | 109.2404 g.                                |
| 15       | 1.0                 | .0461                               | 1.1048                     | .0509                       | 110.9894 g.                                |
| 5        | Water               | .0452                               | 0.9972                     | .0451                       | 100.2209 g.                                |

In order to calculate the volume of the sugar used in making up the solutions, the specified gravity of solid sugar must be known. On looking this up, a wide variation was found in the results obtained by different investigators. It was difficult to decide on which one was correct, so it was decided to work out two tables for each temperature, one using the value 1.5813, obtained independently by Kopp and Gerlack, and the other table based on the value 1.5860 obtained by Schroeder. Joule and Playfair give .0001116 per degree as the cubical expansion of solid sugar between 0 and 100 degrees.

The volume of 1,000 grams of water at the desired temperature was calculated from the values found in Landolt-Boernstein's *Physikalisch-Chemische Tabellen*.

The actual volume of a sugar solution, containing 1,000 grams of water, was calculated from the observed volume and the percentage of water by weight in that volume. The following table 2 gives the percentage by weight of sugar and water in the different concentrations of weight normal sugar solutions.

TABLE 2.

| Weight normal conc. | Weight of water. | Per cent. of water. | Weight of sugar. | Per cent. of sugar. |
|---------------------|------------------|---------------------|------------------|---------------------|
| 0.2                 | 1000             | 93.65               | 67.8784          | 6.35                |
| 0.4                 | 1000             | 88.05               | 135.7568         | 11.95               |
| 0.6                 | 1000             | 83.08               | 203.6352         | 16.92               |
| 0.8                 | 1000             | 78.65               | 271.5136         | 21.37               |
| 1.0                 | 1000             | 74.66               | 339.3920         | 25.34               |

The results obtained at 15 degrees are given in the two following tables. For calculating the volumes of the sugar 1.5813 was used as the specific gravity of solid sugar in table 3 and 1.5860 was used in table 4.

TABLE 3.

Temperature 15 degrees. Sp. Gr. of solid sugar = 1.5813.

| Weight normal conc. | Volume of water. | Volume of sugar | Sum of vols. of water and sugar. | Observed volume. | Difference in vols. in cc. |
|---------------------|------------------|-----------------|----------------------------------|------------------|----------------------------|
| 0.2                 | 1000.857         | 42.924          | 1043.781                         | 1042.949         | 0.832                      |
| 0.4                 | 1000.857         | 85.848          | 1086.705                         | 1084.756         | 1.949                      |
| 0.6                 | 1000.857         | 128.772         | 1129.629                         | 1127.439         | 2.190                      |
| 0.8                 | 1000.857         | 171.696         | 1172.553                         | 1168.358         | 4.195                      |
| 1.0                 | 1000.857         | 214.620         | 1215.477                         | 1210.672         | 4.805                      |

TABLE 4.

Temperature 15 degrees. Sp. Gr. of solid sugar = 1.5860.

| Weight normal conc. | Volume of water. | Volume of sugar. | Sum of vols. of water and sugar. | Observed volume. | Difference in vols. in cc. |
|---------------------|------------------|------------------|----------------------------------|------------------|----------------------------|
| 0.2                 | 1000.857         | 42.788           | 1043.645                         | 1042.949         | 0.696                      |
| 0.4                 | 1000.857         | 85.576           | 1086.433                         | 1084.756         | 1.677                      |
| 0.6                 | 1000.857         | 128.364          | 1129.221                         | 1127.439         | 1.782                      |
| 0.8                 | 1000.857         | 171.152          | 1172.009                         | 1168.358         | 3.651                      |
| 1.0                 | 1000.857         | 213.940          | 1214.797                         | 1210.672         | 4.125                      |

Tables 5 and 6 contain the results obtained at 20 degrees.

TABLE 5.

Temperature 20 degrees. Sp. Gr. of solid sugar = 1.5813.

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1001.751            | 42.948              | 1044.699                               | 1044.007            | 0.692                         |
| 0.4                    | 1001.751            | 85.896              | 1087.647                               | 1065.974            | 1.673                         |
| 0.6                    | 1001.751            | 128.844             | 1130.595                               | 1128.806            | 1.789                         |
| 0.8                    | 1001.751            | 171.792             | 1173.543                               | 1169.877            | 3.666                         |
| 1.0                    | 1001.751            | 214.740             | 1216.491                               | 1212.343            | 4.148                         |

TABLE 6.

Temperature 20 degrees. Sp. Gr. of solid sugar = 1.5860.

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1001.751            | 42.812              | 1044.563                               | 1044.007            | 0.556                         |
| 0.4                    | 1001.751            | 85.624              | 1087.375                               | 1085.974            | 1.401                         |
| 0.6                    | 1001.751            | 128.436             | 1130.187                               | 1128.806            | 1.381                         |
| 0.8                    | 1001.751            | 171.248             | 1172.999                               | 1169.877            | 3.122                         |
| 1.0                    | 1001.751            | 214.060             | 1215.811                               | 1212.343            | 3.468                         |

Tables 7 and 8 contain the results obtained at 25 degrees.

TABLE 7.

Temperature 25 degrees. Sp. Gr. of solid sugar = 1.5813.

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1002.911            | 42.972              | 1045.883                               | 1045.307            | 0.576                         |
| 0.4                    | 1002.911            | 85.944              | 1088.855                               | 1087.417            | 1.438                         |
| 0.6                    | 1002.911            | 128.916             | 1131.827                               | 1130.412            | 1.415                         |
| 0.8                    | 1002.911            | 171.888             | 1174.799                               | 1171.596            | 3.203                         |
| 1.0                    | 1002.911            | 214.860             | 1217.771                               | 1214.209            | 3.562                         |



TABLE 8.

Temperature 25 degrees. Sp. Gr. of solid sugar = 1.5860.

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1002.911            | 42.836              | 1045.747                               | 1045.307            | 0.440                         |
| 0.4                    | 1002.911            | 85.672              | 1088.583                               | 1087.417            | 1.116                         |
| 0.6                    | 1002.911            | 128.508             | 1131.409                               | 1130.412            | .997                          |
| 0.8                    | 1002.911            | 171.344             | 1174.255                               | 1171.596            | 2.659                         |
| 1.0                    | 1002.911            | 214.180             | 1217.090                               | 1214.209            | 2.881                         |

Tables 9 and 10 contain the results obtained at 30 degrees.

TABLE 9.

Temperature 30 degrees. Sp. Gr. of solid sugar = 1.5813.

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1004.314            | 42.994              | 1047.308                               | 1046.801            | 0.507                         |
| 0.4                    | 1004.314            | 85.988              | 1090.302                               | 1089.055            | 1.247                         |
| 0.6                    | 1004.314            | 128.982             | 1132.296                               | 1132.182            | 1.114                         |
| 0.8                    | 1004.314            | 171.976             | 1176.290                               | 1173.479            | 2.811                         |
| 1.0                    | 1004.314            | 214.970             | 1219.284                               | 1216.235            | 3.049                         |

TABLE 10.

Temperature 30 degrees. Sp. Gr. of solid sugar = 1.5860

| Weight<br>normal conc. | Volume of<br>water. | Volume of<br>sugar. | Sum of vols.<br>of water<br>and sugar. | Observed<br>volume. | Difference in<br>vols. in cc. |
|------------------------|---------------------|---------------------|----------------------------------------|---------------------|-------------------------------|
| 0.2                    | 1004.314            | 42.860              | 1047.174                               | 1046.801            | 0.373                         |
| 0.4                    | 1004.314            | 85.720              | 1090.034                               | 1089.055            | 0.979                         |
| 0.6                    | 1004.314            | 128.580             | 1132.894                               | 1132.182            | 0.712                         |
| 0.8                    | 1004.314            | 171.440             | 1175.754                               | 1173.479            | 2.275                         |
| 1.0                    | 1004.314            | 214.300             | 1218.614                               | 1216.235            | 2.379                         |

The values of the contraction obtained at the different temperatures are all brought together in Tables 11 and 12, in order to observe what takes place as the temperature is raised.

TABLE 11.

Sp. Gr. of solid sugar = 1.5813.

| Weight<br>normal conc. | Contraction<br>at 15°. | Contraction<br>at 20°. | Contraction<br>at 25°. | Contraction<br>at 30°. | Decrease in<br>contraction |
|------------------------|------------------------|------------------------|------------------------|------------------------|----------------------------|
| 0.2                    | 0.832                  | 0.692                  | 0.576                  | 0.507                  | .325                       |
| 0.4                    | 1.949                  | 1.673                  | 1.438                  | 1.247                  | .702                       |
| 0.6                    | 2.190                  | 1.789                  | 1.415                  | 1.114                  | 1.079                      |
| 0.8                    | 4.195                  | 3.666                  | 3.203                  | 2.811                  | 1.384                      |
| 1.0                    | 4.805                  | 4.148                  | 3.562                  | 3.049                  | 1.756                      |

TABLE 12.

Sp. Gr. of solid sugar = 1.5860.

| Weight<br>normal conc. | Contraction<br>at 15°. | Contraction<br>at 20°. | Contraction<br>at 25°. | Contraction<br>at 30°. | Decrease in<br>contraction<br>between<br>15° and 30°. |
|------------------------|------------------------|------------------------|------------------------|------------------------|-------------------------------------------------------|
| 0.2                    | 0.696                  | 0.556                  | 0.440                  | 0.373                  | .323                                                  |
| 0.4                    | 1.677                  | 1.401                  | 1.116                  | 0.979                  | .698                                                  |
| 0.6                    | 1.782                  | 1.381                  | .997                   | 0.712                  | 1.060                                                 |
| 0.8                    | 3.651                  | 3.122                  | 2.659                  | 2.275                  | 1.376                                                 |
| 1.0                    | 4.125                  | 3.468                  | 2.881                  | 2.379                  | 1.756                                                 |

A study of the table shows that as the temperature is raised, the contraction, or the difference between the sum of the volumes of the solute and solvent on the one side, and the observed volume of the solution on the other side, diminishes. This decrease is not directly proportional to the rise in temperature, but is greater between 15 and 20 degrees than it is between 20 and 25 or 25 and 30 degrees. At each temperature, the contraction is proportional to the concentration, as is also the decrease in contraction. Sufficient data is not at hand to pass final judgment on these facts, but it appears that as the temperature is raised, the observed volumes approaches that of the sum of the volumes of the solvent and solute. Whether or not they ever become equal remains for future investigations to show. The two most concentrated so-

lutions were found to have lost in rotation while they were in the bath, but lack of time prevented repetition of the experiments. The exact rotations in degrees are given in Table 13. The first column gives the rotation when the solution was made up, the second column, the rotation when the apparatus was taken down after the completion of the experiment, and the last column, the loss in rotation.

TABLE 13.

| Weight<br>normal conc. | Rotation<br>before<br>experiment. | Rotation<br>after<br>experiment. | Loss in<br>rotation |
|------------------------|-----------------------------------|----------------------------------|---------------------|
| 0.2                    | 24.85                             | 24.80                            | 0.05                |
| 0.4                    | 48.0                              | 47.8                             | 0.2                 |
| 0.6                    | 69.2                              | 69.2                             | 0.00                |
| 0.8                    | 89.0                              | 84.3                             | 4.7                 |
| 1.0                    | 107.4                             | 98.8                             | 8.6                 |

It is known<sup>1</sup> a loss of one degree in rotation corresponds, in the case of .9 weight normal cane sugar solution at 20 degrees C. to 2.49 grams of invert sugar, and in the case of 1.0 weight normal sugar solution to 2.53 grams of invert sugar. This correction could be applied as a means of ascertaining the extent of the inversion of the cane sugar; if it could be proved that none of the products of the inversion had been converted by fermentation into carbon dioxide and water.

The expansion coefficients for the solutions between the different temperatures were also calculated. Table 14 contains the expansion coefficients between 15 and 20 degrees, based on the volumes of the solutions at 15 degrees as unity. It also contains the volume and expansion coefficient of air-free water reduced to the same unit i. e. the volume of water at 15 degrees.

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1. Dissertation of E. J. Hoffman, 1906.

TABLE 14.

| Weight<br>normal conc. | Volume<br>at 15°. | Volume<br>at 20°. | Increase in<br>volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.4096          | 100.4976          | .0880                  | .000175                    |
| 0.2                    | 100.2520          | 100.3536          | .1017                  | .000203                    |
| 0.4                    | 100.4023          | 100.5150          | .1128                  | .000224                    |
| 0.6                    | 100.4419          | 100.5637          | .1218                  | .000243                    |
| 0.8                    | 100.3826          | 100.5130          | .1305                  | .000260                    |
| 1.0                    | 100.3220          | 100.4605          | .1385                  | .000276                    |

Table 15 contains the expansion coefficients of the sugar solutions, also air-free water between 20 and 25 degrees, based on the volumes at 20 degrees as unity.

TABLE 15.

| Weight<br>normal conc. | Volume<br>at 20°. | Volume<br>at 25°. | Increase in<br>volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.4976          | 100.6132          | .1156                  | .000230                    |
| 0.2                    | 100.3536          | 100.4786          | .1249                  | .000249                    |
| 0.4                    | 100.5150          | 100.6486          | .1335                  | .000266                    |
| 0.6                    | 100.5637          | 100.7067          | .1430                  | .000284                    |
| 0.8                    | 100.5130          | 100.6607          | .1477                  | .000294                    |
| 1.0                    | 100.4605          | 100.6151          | .1546                  | .000308                    |

Table 16 contains the expansion coefficients of the sugar solutions, also air-free water between 25 and 30 degrees, based on the volumes at 25 degrees as unity.

TABLE 16.

| Weight<br>normal conc. | Volume<br>at 25°. | Volume<br>at 30°. | Increase in<br>volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.6132          | 100.7507          | .1375                  | .000274                    |
| 0.2                    | 100.4786          | 100.6222          | .1436                  | .000286                    |
| 0.4                    | 100.6486          | 100.8002          | .1516                  | .000301                    |
| 0.6                    | 100.7067          | 100.8644          | .1577                  | .000313                    |
| 0.8                    | 100.6607          | 100.8225          | .1618                  | .000322                    |
| 1.0                    | 100.6151          | 100.7829          | .1678                  | .000334                    |



All the coefficients are brought together in Table 17 for the sake of comparison.

TABLE 17.

| Weight<br>normal conc. | Expansion<br>coefficients<br>15°—20°. | Expansion<br>coefficients<br>20°—25°. | Expansion<br>coefficients<br>25°—30°. |
|------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| Water                  | .000175                               | .000230                               | .000274                               |
| 0.2                    | .000203                               | .000249                               | .000286                               |
| 0.4                    | .000224                               | .000266                               | .000301                               |
| 0.6                    | .000243                               | .000284                               | .000313                               |
| 0.8                    | .000260                               | .000294                               | .000322                               |
| 1.0                    | .000276                               | .000308                               | .000334                               |

In the preceding expansion coefficients, the ones obtained between 15 and 20 degrees are referred to the volume of the solution at 15 degrees as unity, those between 20 and 25 degrees are referred to the volume at 20 degrees as unity, and those between 25 and 30 degrees are referred to the volume at 25 degrees as unity. It seemed desirable to calculate the expansion coefficients basing them all on the same unit. In the following, then, the unit employed is the volumes of the solutions at 15 degrees, and in the case of air-free water, the volume of the water at 15 degrees.

Table 18 contains the expansion coefficients between 15 and 20 degrees.

TABLE 18.

| Weight<br>normal conc. | Volume<br>at 15°. | Volume<br>at 20°. | Increase<br>in volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.4096          | 100.4976          | .0880                  | .000175                    |
| 0.2                    | 100.2520          | 100.3536          | .1017                  | .000203                    |
| 0.4                    | 100.4023          | 100.5150          | .1128                  | .000224                    |
| 0.6                    | 100.4419          | 100.5637          | .1218                  | .000243                    |
| 0.8                    | 100.3826          | 100.5130          | .1305                  | .000260                    |
| 1.0                    | 100.3220          | 100.4605          | .1385                  | .000276                    |

Table 19 contains the expansion coefficients between 20 and 25 degrees, based on the volume at 15 degrees as unity.

TABLE 19.

| Weight<br>normal conc. | Volume<br>at 20°. | Volume<br>at 25°. | Increase<br>in volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.4976          | 100.6132          | .1156                  | .000230                    |
| 0.2                    | 100.3536          | 100.4786          | .1249                  | .000249                    |
| 0.4                    | 100.5150          | 100.6486          | .1335                  | .000266                    |
| 0.6                    | 100.5637          | 100.7067          | .1430                  | .000285                    |
| 0.8                    | 100.5130          | 100.6607          | .1477                  | .000295                    |
| 1.0                    | 100.4605          | 100.6151          | .1546                  | .000308                    |

Table 20 contains the expansion coefficients between 25 and 30 degrees, based on the volume at 15 degrees as unity.

TABLE 20.

| Weight<br>normal conc. | Volume<br>at 25°. | Volume<br>at 30°. | Increase<br>in volume. | Expansion<br>coefficients. |
|------------------------|-------------------|-------------------|------------------------|----------------------------|
| Water                  | 100.6132          | 100.7507          | .1375                  | .000274                    |
| 0.2                    | 100.4786          | 100.6222          | .1436                  | .000286                    |
| 0.4                    | 100.6486          | 100.8002          | .1516                  | .000301                    |
| 0.6                    | 100.7067          | 100.8644          | .1577                  | .000315                    |
| 0.8                    | 100.6607          | 100.8225          | .1618                  | .000322                    |
| 1.0                    | 100.6151          | 100.7829          | .1678                  | .000344                    |

All the expansion coefficients, based on the volumes at 15 degrees, are brought together in Table 21.

TABLE 21.

| Weight<br>normal conc. | Expansion<br>coefficients<br>15°—20°. | Expansion<br>coefficients<br>20°—25°. | Expansion<br>coefficients<br>25°—30°. |
|------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| Water                  | .000175                               | .000230                               | .000274                               |
| 0.2                    | .000203                               | .000249                               | .000286                               |
| 0.4                    | .000224                               | .000266                               | .000301                               |
| 0.6                    | .000243                               | .000285                               | .000315                               |
| 0.8                    | .000260                               | .000295                               | .000322                               |
| 1.0                    | .000276                               | .000308                               | .000344                               |

The expansion coefficients increase with the temperature, as shown by the table. They are also roughly proportional to the concentration, but the results can not be regarded as final since the 0.8 and 0.9 weight normal solutions lost in rotation. This portion of the work will therefore have to be repeated.

The expansion coefficients obtained for water show practical agreement with those given in Landolt-Boernstein's *Physikalisch-Chemische Tabellen*, so that the apparatus may be regarded as accurate. With apparatus on hand, then, the volumes of various solutions can be determined over a considerable range of temperature, and some light may be thrown on facts whose relation at present is not clearly seen.



### BIOGRAPHY.

Felton Samuel Dengler was born May 19, 1886, at Steelton, Pennsylvania. His early education was obtained from the public schools of that place. He entered Pennsylvania College in the fall of 1905, and graduated with the B. S. degree in 1909. In October, 1909, he entered the Chemical Department of Johns Hopkins University. His subordinate subjects are Physical Chemistry and Applied Electricity.









